

EFFECT OF PORE STRUCTURE OF Ni-Mo CATALYSTS ON HYDROCRACKING OF ASPHALTENE AND PREASPHALTENE AND HETEROATOM REMOVAL

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INTRODUCTION

Catalytic upgrading of coal liquids is an important step in two-stage coal liquefaction. This process is still confronted with the problem of achieving high catalyst performance for efficient conversion of heavy materials. A number of previous works showed the importance of catalyst pore structure in coal liquefaction (1-3) and in hydroprocessing of petroleum residues due to diffusional limitations (4-7). Several reports on hydrotreating of coal liquids (8-10) suggested that large pore catalysts are effective in converting 450°C+ fractions. Our preliminary results showed that the pore size of Mo catalysts supported on silica or alumina affects the conversion of asphaltene and preasphaltene (11-13).

The major purpose in upgrading primary coal liquids is to convert the heavy materials such as asphaltene and preasphaltene into oils (hexane solubles) with low heteroatom content, which can be used as feed for further refining by conventional petroleum processing technology. The knowledge on the catalyst pore size effect for converting coal-derived asphaltene and preasphaltene is still very limited. This work aimed at clarifying the effects of pore size of Ni-Mo catalysts on their performance in converting the heavy materials and in heteroatom removal. The results and mechanistic considerations are reported in this paper.

EXPERIMENTAL

The catalyst supports were cylindrical gamma-alumina extrudate prepared from boehmite gel (Table 1), which were provided by Sumitomo Metal Mining Co. (S-1), the Catalyst Society of Japan (S-2), and Chiyoda Chemical Engineering and Construction Co. (S-3 and S-4). The catalysts were prepared by co-impregnation of ammonium heptamolybdate and nickel nitrate from their aqueous solution, in which 25% aqueous ammonia was added to give a homogeneous solution, followed by evaporation under reduced pressure. The impregnated extrudates were then dried at 250°C for 2 h in a tube furnace (to remove adsorbed water) and calcined at 500°C for 5 h in an air flow. The catalysts were sulfided (11) and kept in hexane before use. Table 1 gives the physical properties, and Figure 1 shows the pore size distribution of the four Ni-Mo/Al₂O₃ catalysts prepared by using the same procedure. The pore size distribution was measured by using a Shimadzu AutoPore-9200 mercury porosimeter. A commercial KF-153S sulfided Ni-Mo/Al₂O₃ (14) catalyst (Cat-C) was also used in some experiments. The prepared catalysts have the same contents of Ni and Mo to those of the commercial Cat-C (NiO: 2.9, MoO₃: 15.8 wt%). The size of the available extrudates was 1.5 mm (d) for Cat-1, Cat-2 and Cat-C, and 0.8 mm for Cat-3 and Cat-4. In practice, the lowest catalyst sizes permitted in industrial fixed-bed operations are 0.8-1.6 mm.

Table 2 gives the sources and properties of the feed samples, in which Wan-SRC and Aka-SRC were produced from Wandoan subbituminous coal (at 440°C) and Akabira bituminous coal (at 420°C) in a coal liquefaction plant at Sumitomo Coal Mining Co. (11). The coal-derived asphaltenes, Aka-Asp and Wan-Asp (hexane-insoluble benzene solubles) and preasphaltene (Wan-Preasp) were separated from the corresponding SRC. The bitumen asphaltene (Aosb-Asp) was separated from Athabasca oil sand bitumen (12). The original asphaltenes were analyzed by using gel permeation chromatography, GPC (14-15) and ¹H NMR (16-17). The hydrocracking was carried out in a 60 ml rocking autoclave at 425°C for 1 h with 4.9 MPa H₂ (cold). Tetralin was used as solvent unless otherwise mentioned (5g feed/0.5g cylindrical catalyst/5g solvent). The products were separated into gases, oils (hexane solubles), asphaltene, and benzene insolubles, BI (15). The gases were analyzed by GC (Shimadzu 9A). The H₂S in gases were analyzed by using H₂S indicator tube (Kitagawa Indicator) at room temperature.

RESULTS AND DISCUSSION

Asphaltene Structure and Reactivity

Structure of Asphaltene. Table 3 gives the NMR results. As can be seen from Tables 2-3, the coal-derived asphaltenes, Aka-Asp and Wan-Asp have higher C, O and N contents, higher aromaticity and lower H/C atomic ratios, while the bitumen asphaltene (Aosb-Asp) has higher H and S contents, higher H/C ratio and lower aromaticity. Aka-Asp and Wan-Asp contain more aromatic hydrogens (Har), whereas Aosb-Asp is rich in aliphatic hydrogens present in long alkyl side-chains and naphthenic groups (Table 3). The size distribution of the asphaltenes was evaluated by GPC. Figure 2 shows the GPC results, in which the molecular size decreases with increase in elution (retention) time. The broad GPC curves of Aka-Asp and Wan-Asp show that they consist of various components ranging from relatively small to large molecules. The peak sizes correspond to a molecular weight (MW) range of about 200-1000. On the other hand, Aosb-Asp shows a sharp GPC peak in the range of much larger molecular sizes, corresponding to peak MW values of at least over 1000. The average MW values are in the range of 400-600 for Aka-Asp, Wan-Asp and other coal-derived asphaltenes (12,18), and 3000-6000 for Aosb-Asp and other bitumen and petroleum asphaltenes (12,19). These results showed that most coal-derived asphaltene molecules have smaller size and lower MW than bitumen and petroleum asphaltenes.

Reactivity of Asphaltene. Table 4 presents the data on asphaltene reactivity. The thermal run of coal-derived Aka-Asp in H₂-tetralin gave similar conversion to that of the bitumen asphaltene Aosb-Asp. However, the oil yield was lower, and the amount of BI formed from retrogressive reactions was higher with Aka-Asp. The run of Wan-Asp was also accompanied by considerable BI formation. The effect of tetralin in suppressing retrogressive reactions was evaluated by the runs using decalin. The BI from Aka-Asp increased from 9.7 to 12.2% when the solvent changed from H-donor tetralin to decalin, whereas there was little change in BI from Aosb-Asp (1.8 vs. 1.9%). These results showed that coal-derived asphaltenes have high thermal reactivity which also leads to remarkable retrogressive reactions to form BI. Probably the BI formation involved the crosslinking and condensation of reactive radicals and some unstable compounds, especially hydroxy compounds which are rich in coal-derived asphaltenes (18,20) and tend to undergo coupling reactions to form more refractory materials (21-22). As shown in Table 4, H₂S was also formed in the thermal runs, and considerable amounts of H₂S were produced from Aosb-Asp both in tetralin and in decalin. From these results, it seems that thermal decomposition of the bitumen asphaltene involved the cleavage of weak C-C and aliphatic C-S bonds (23), and the resulting radicals were readily stabilized in H₂-solvent systems to form oils, C₁-C₄ and H₂S.

Catalytic Conversion of Asphaltene and Preasphaltene

Catalyst Properties. With an attempt to examine the effects of catalyst pore size on an unified basis, we prepared four Ni-Mo catalysts using pure gamma-alumina supports. As can be seen from Figure 1 and Table 1, each of the four prepared Ni-Mo catalysts exhibits an unimodal distribution of pore sizes within a specific range. The median pore diameter (MPD) increases in the order of Cat-1 (120 Å) < Cat-2 (150 Å) < Cat-3 (290 Å) < Cat-4 (730 Å). The surface area, however, decreases as pore size increases. The unimodal pore structure and the significantly different pore sizes of Cat-1 through Cat-4 prepared by using the same procedure, enabled us to evaluate the pore size effects.

Asphaltene Hydrocracking. Figure 3 shows the distribution of products from hydrocracking of a coal-derived asphaltene, Aka-Asp. The catalysts significantly promoted Aka-Asp conversion and increased oil yields from 50.7% to more than 69%, without increase in gas yields. The catalysts also reduced BI from 9.7% to less than 3%. Figure 4 shows the conversions and product yields as a function of catalyst pore size (MPD). It is clear from Figure 4 that the conversions of Aka-Asp and oil yields increased remarkably with increase in catalyst MPD up to 290 Å, in spite of the decrease in catalyst surface area with increasing MPD. On the other hand, further increase in MPD from 290 to 730 Å did not offer any advantage. We also examined the solvent effect in the catalytic runs of Aka-Asp with Cat-1 and Cat-3. Using decalin instead of tetralin resulted in 1-2% more BI and slightly higher H₂ consumption. The amounts of BI formed in both cases were lower with large pore Cat-3 than with small pore Cat-1.

Figure 5 presents the results for hydrocracking of Aosb-Asp. The conversions and yields of oils plus gases increased with MPD up to 290 Å, while further increasing MPD to 730 Å decreased the conversion. In this case, catalysts also enhanced the formation of BI and gases. The amounts of H₂S formed in gas phase changed remarkably with different catalysts. The detected H₂S (ml at 25°C under ambient pressure) amounts were as follows: none (26.9) < Cat-1 (45.5) < Cat-2 (52.5) < Cat-3 (77.8) > Cat-4 (34.4). Because of the low S content of Aka-Asp (0.5%) as compared to that of Aosb-Asp (8.3%), the amounts of detected H₂S were much smaller, within 2-4 ml (Cat-1: 3.7; Cat-2: 2.0; Cat-3: 1.8; Cat-4: 1.9).

Since the sizes of the bitumen asphaltene molecules are very large (Figure 2), it might be expected that their conversion might be more sensitive to catalyst pore size. Nevertheless, the increasing extents of oil yields and conversions with MPD were higher with the coal-derived Aka-Asp (Figure 4). Moreover, the highest oil yield from Aosb-Asp with the largest-pore Cat-4 (69.4%) was still lower by 11% than that from Aka-Asp with Cat-3 (80.4%). This comparison suggests that the conversion of coal-derived asphaltenes is sensitive to catalyst pore size although their molecular sizes are, on average, much smaller than bitumen and petroleum asphaltenes. In addition, the catalytic runs of Aka-Asp consumed slightly more H₂ (2.1-2.3wt%) than the corresponding runs of Aosb-Asp (1.9-2.2wt% based on asphaltene). In both cases, H₂ consumptions with large pore Cat-3 were slightly higher than with small pore Cat-1.

Preasphaltene Hydrocracking. Preasphaltene is also a major fraction in primary coal liquids. Figure 6 presents the results for a coal-derived preasphaltene, Wan-Preasp using Cat-1, Cat-3 and Cat-4. The yields of asphaltenes and recovered benzene insolubles were 24.8 and 41.2% with Cat-1, 30.1 and 34.4% with Cat-3, and 33.1 and 29.5% with Cat-4. Apparently, asphaltene yields increased with increasing catalyst MPD from 120 Å (Cat-1) up to 730 Å (Cat-4), rather than a decreasing trend as would be anticipated from the results with the asphaltene fraction as feed (Figure 4). These results suggest that the effect of catalyst pore size on product distribution also depends on the feed used.

SRC Hydroprocessing. Figure 7 presents the results for the unfractionated Wan-SRC, which contained each of the following fractions: oils (35.7%), asphaltene (33.1%) and preasphaltene (31.2%). In this case, we also used a sulfided commercial KF-153S Ni-Mo catalyst (Cat-C, Table 1), which has a MPD value similar to that of the well known Shell 324M Ni-Mo (90 vs. 86 Å). It should be noted that Cat-1 though Cat-4 is alumina-supported catalyst, while Cat-C contains 4.5wt% SiO₂. Figure 8 shows the results for Aka-SRC which contained more preasphaltene (41.5%) and less asphaltene (27.0%) and oils (31.5%) as compared to Wan-SRC. As can be seen from Figures 7 and 8, the yields of preasphaltene decreased with increasing MPD. The oil yields from both SRC increased with MPD up to 290 Å. The gas yields were nearly constant in the runs of Wan-SRC (3.6-4.6%) and Aka-SRC (4.3-5.0%).

Figure 9 shows the effect of catalyst pore size on the net conversion of the heavy materials during SRC hydroprocessing. For runs of both Wan-SRC and Aka-SRC, increasing catalyst pore size significantly promoted preasphaltene conversion. This is consistent with the results shown in Figure 6 for runs of the isolated preasphaltene fraction. It is interesting to note that increasing MPD above certain sizes caused decrease in asphaltene conversion during the runs of the whole SRC (Figure 9). This is considerably different from the trend observed in the runs of isolated asphaltene fraction, where increasing MPD remarkably promoted asphaltene conversion and oil yields (Figure 4). The net conversion of the heavy fractions, especially asphaltene, also appeared to be lower in the runs of unfractionated SRC.

Combination of the results in Figures 3-4 and in Figures 6-9 revealed that in SRC upgrading, when the catalyst pores exceeded certain sizes, more preasphaltene molecules which have larger sizes than asphaltenes will diffuse into pores and react on catalyst surface, producing more asphaltene. There is no doubt that increasing pore size also facilitates the diffusion and reaction of asphaltene fractions (Figures 3-5), but the first step of catalytic conversion is adsorption. As the pore sizes become large enough to allow the diffusion of larger molecules, preasphaltene tend to adsorb on the catalyst surface in preference to asphaltene, probably because of the higher aromaticity and higher polarity of the former. The present results were obtained with cylindrical extrudate catalysts. Previous works showed that the change in the extrudate size within the range of 1.6 to 0.8 mm does not have any significant effect on initial activity, while the <100 mesh fine particles generally afford higher conversions than extrudates (24), which is another indication of the diffusional limitations occurring during SRC hydroprocessing.

Heteroatom Removal

Relative to the thermal runs, the Ni-Mo catalysts increased H contents and H/C ratios, and decreased heteroatom contents; the oils from coal-derived materials have lower H/C ratios (1.01-1.05) than those (1.36-1.39) from the bitumen asphaltene (24). Using the catalysts with different pore sizes caused considerable differences in O contents of the products from coal-derived materials and the recovered asphaltenes from Aosb-Asp, and in S contents of both oils and asphaltenes from Aosb-Asp, indicating the importance of catalyst pore size in hydrodeoxygenation (HDO) and hydrodesulfurization (HDS).

Figure 10 shows the O contents of products from Aka-Asp and Wan-SRC and those of recovered asphaltenes from Aosb-Asp as a function of catalyst MPD. There is little or no literature information relating to the effect of catalyst pore size on HDO of coal liquids and bitumen or petroleum. In this work, the analytical results for Aka-Asp and Aosb-Asp were confirmed by repeated analyses of samples from duplicated runs. The maximum HDO degree of given products corresponds to the lowest O contents. As can be seen from Figure 10, the MPD values of 120 Å (Cat-1) and 150 Å (Cat-2) correspond to higher HDO degree of oils, while the latter was superior (to the former) for HDO of asphaltenes where a maximum HDO was achieved in the cases of both Aka-Asp and Aosb-Asp. When SRC was the feed (Wan-SRC), the MPD range corresponding to higher HDO degrees of asphaltenes appeared to become wider or larger. Combining the results in Figures 1 and 10 suggests that 80-160 Å pores with a peak around 120 Å are effective for HDO of oils, while 100-200 Å (MPD: 150 Å) pores are preferable for HDO of asphaltenes.

In Figure 11 the S contents of oils and asphaltenes as well as the amounts of H₂S formed from the sulfur-rich Aosb-Asp were plotted against the catalyst MPD. Unlike HDO of Aosb-Asp, its HDS degree reached a maximum at catalyst MPD of 290 Å (Cat-3), which corresponds to the lowest S contents of products and the highest H₂S amount in gas. Sulfur is also the major heteroatom in petroleum, and there are many reports on HDS of petroleum crudes and heavy oils including the effect of pore size (4-7). In the catalytic runs of the coal-derived sulfur-less Aka-Asp, no difference in HDS was apparent, because all the catalysts completely removed sulfur from the products (24). Bertolacini et al.(1) showed that in the liquefaction of a high-sulfur coal using Co-Mo catalysts (60-100 mesh), the higher activities for HDS and coal conversion correspond to MPD of 100-120 Å and about 200 Å, respectively.

The HDO and HDS results can be explained in terms of relation between pore size and surface area, and competitive adsorption and reaction on catalyst surface. It is considered that there are two main paths for heteroatom removal: simultaneous asphaltene conversion and heteroatom removal, and HDO/HDS of formed or originally present oils and asphaltenes. By applying the molecular size distribution concept as suggested by GPC (Figure 2), one anticipates that the smaller pores contribute to HDS and HDO of small molecules, and larger pores promote the reactions of large molecules. Large pores facilitate the diffusion of large molecules, whereas the large pore catalysts possess lower surface area which lowers the activity on catalyst weight basis. The results for runs of coal-derived materials (Figures 4,6,9) suggest that pore size change also affects the competition between adsorption of different compounds/fractions, and heavier molecules such as those in preasphaltene tend to adsorb in preference, which partially inhibits the conversion of less heavier asphaltene molecules. As long as the molecules can diffuse fast enough into the interior of the pores and can adsorb on the active sites, the degrees of HDO and HDS are then determined mainly by the area and intrinsic activity of the catalysts. Therefore, the existence of different ranges of preferable pore sizes for different reactions and for different feed materials is due to the interdependence between pore size, surface area, and competitive adsorption/reaction.

It is expected that there is difference in catalyst dispersion. With the chemically identical supports, the catalyst dispersion should increase with surface area. One can hardly see any effect in the observed trends with Cat-1, Cat-2 and Cat-3 that might be attributed to different dispersion. However, the generally lower HDS and HDO activities of the largest pore Cat-4 may be due in part to its lowest surface area, and poor dispersion of Ni-Mo active phase. On the other hand, there was little decrease in N content of products, probably because of the mild conditions (low H₂ pressure, 4.9 MPa). Siegel et al.(8) reported that higher metal loadings and larger pores appear to yield some improvement in HDN. In addition, HDN over conventional Ni-Mo and Co-Mo catalysts is known to be more difficult than HDO and HDS, and requires extensive hydrogenation. Shabtai et al. (25) and Hirschon et al. (26) have found that adding Ru to alumina-supported Mo catalysts can improve HDN selectivity.

CONCLUSIONS

1. The performance of unimodal Ni-Mo catalysts for asphaltene and preasphaltene conversion and for oxygen and sulfur removal at 425°C with 4.9 MPa H₂ appeared to depend on their pore size distribution.
2. In the runs of isolated heavy fractions, the conversions increased with catalyst MPD up to 290 Å, and further MPD increase to 730 Å did not offer apparent advantage for converting coal- and oil sand bitumen-derived asphaltenes, but had positive effect in the runs of coal-derived preasphaltene.
3. Relative to the bitumen asphaltene, the sizes of most coal derived asphaltenes are much smaller, but their conversions are sensitive to catalyst pore size. The thermal conversion of coal-derived asphaltenes is accompanied by remarkable retrogressive reactions, even in the presence of H-donor solvent. When the large pore catalyst (MPD: 290 Å) was used, these materials can be converted into oils in high yields under mild conditions, while the oils have lower H/C ratios than those from the bitumen asphaltene.
4. In the hydroprocessing of unfractionated primary coal liquids which contain preasphaltene in addition to asphaltene and oils (SRC), increasing catalyst pore size significantly promoted preasphaltene conversion, producing more asphaltene. In this case, the use of large pore catalysts seems to decrease the net conversion of asphaltene fraction.
5. The preferable pore size ranges, which may not be the optimum, appeared to be 80-160 Å with a peak MPD around 120 Å for HDO (oxygen removal) of oils, and 100-200 Å with a peak MPD around 150 Å for HDO of asphaltenes. Maximum HDS (sulfur removal) of the sulfur-rich bitumen asphaltene was observed at MPD of 290 Å which corresponds to a pore size range of 200-400 Å.

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Table 1. Properties of Supports and Sulfided Ni-Mo Catalysts

Properties	Al ₂ O ₃ supports ^a				Ni-Mo/Al ₂ O ₃ catalysts ^b				
	S-1	S-2	S-3	S-4	Cat-1	Cat-2	Cat-3	Cat-4	Cat-C ^c
Median pore diam., Å	115	120	280	750	120	150	290	730	90
Surface area, m ² /g	203	174			152	128	126	80	255
Pore volume, ml/g	0.79	0.65	1.05	1.49	0.49	0.45	0.84	1.01	0.56

a) Data received; b) Measured for prepared catalysts; c) Commercial KF-153S-1.5E Ni-Mo/Al₂O₃; Metal loading in Cat-1 to Cat-4 and Cat-C, MoO₃: 15.8, NiO: 2.9 wt%.

Table 2. Elemental Analysis of Coal- and Bitumen-Derived Asphaltene and SRC

Asphaltene & SRC	Elemental (wt%)					Atomic H/C	Source and content		
	C	H	N	S	O ^a		Origin	Source	wt%
Aka-Asp	83.8	6.1	2.0	0.5	7.6	0.87	Akabira Coal	SRC	27.1
Wan-Asp	84.3	6.0	1.6	0	8.1	0.86	Wandoan Coal	SRC	33.1
Aosb-Asp	80.1	8.0	1.2	8.3	2.4	1.20	Ath. Oil Sand	Bitumen	15.0
Wan-Preasp	83.0	5.0	2.0	0	10.0	0.72	Wandoan Coal	SRC	31.2
Wan-SRC	85.7	6.1	1.5	0	6.7	0.85	Wandoan Coal	SRC	100.0
Aka-SRC	84.9	6.2	1.8	0.3	6.8	0.87	Akabira Coal	SRC	100.0

a) By difference.

Table 3. ¹H NMR Analysis of Coal- and Bitumen-Derived Asphaltenes

Asphaltene	H distribution per 100 C atoms ^a						Aromaticity f _a
	H _{ar}	H _{n-CH2} ^b	H _{w-CH2}	H _{w-CH3}	H _{f-CH2}	H _{f-CH3} ^c	
Aka-Asp	28.0	6.0	17.2	7.2	7.9	14.0	0.74
Wan-Asp	30.6	5.1	14.8	6.9	7.1	15.6	0.77
Aosb-Asp	9.6	5.5	15.1	7.3	11.9	41.1	0.58

a) Based on ¹H NMR and elemental analysis; b) Methylene H α to two aromatic rings; c) Includes β-CH₃ and methylene H γ or further from an aromatic ring; d) Methyl H γ or further from an aromatic ring.

Table 4. Reactivity of Asphaltenes in Non-Catalytic Hydrocracking

Solvent	Tetralin			Decalin	
	Aka-Asp	Wan-Asp	Aosb-Asp	Aka-Asp	Aosb-Asp
Products (wt%)					
Gas	5.7	4.8	4.2	4.9	6.5
Oil	50.7	49.0	59.4	50.6	58.2
Asphaltene	33.9	37.7	34.6	32.3	33.4
BF	9.7	8.5	1.8	12.2	1.9
H ₂ S in gas (ml)	2.7	1.1	26.9	1.0	20.1
Conversion (wt%)	66.1	62.3	65.4	67.7	66.6
H ₂ consumption (wt%)	0.5	0.6	0.9	0.9	1.1

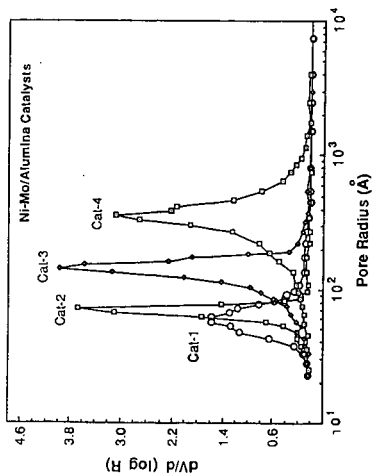


Figure 1. Pore size distribution of prepared Ni-Mo/Al₂O₃ catalysts

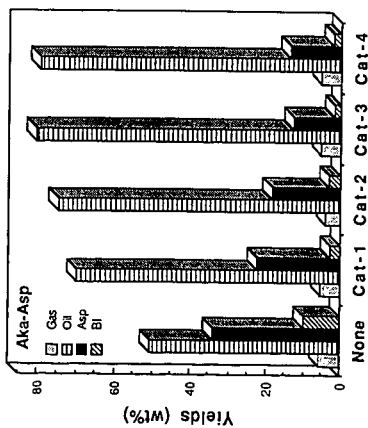


Figure 3. Effect of Ni-Mo catalysts in Aka-Asp hydrocracking

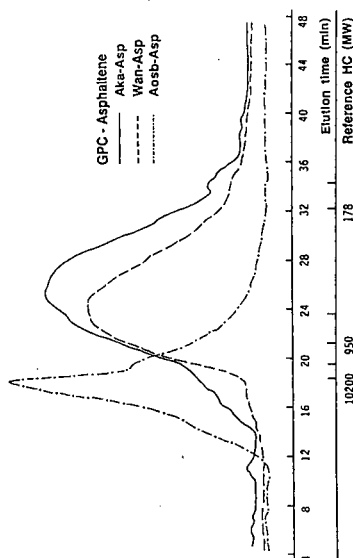


Figure 2. Gel permeation chromatograms of asphaltenes using CHCl₃ as mobile phase

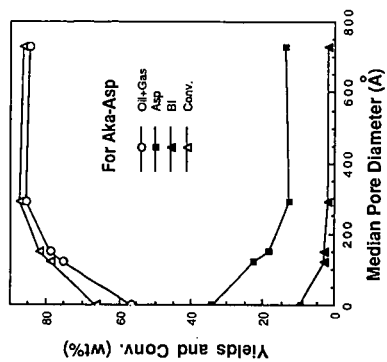


Figure 4. Effect of catalyst pore size on hydrocracking of coal-derived asphaltene

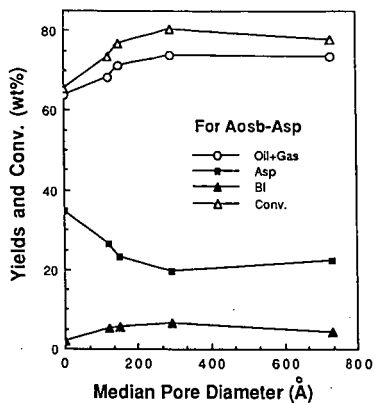


Figure 5. Effect of catalyst pore size on hydrocracking of oil sand bitumen-derived asphaltene

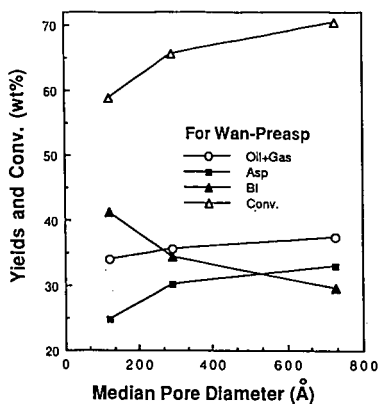


Figure 6. Effect of catalyst pore size on hydrocracking of coal-derived preasphaltene

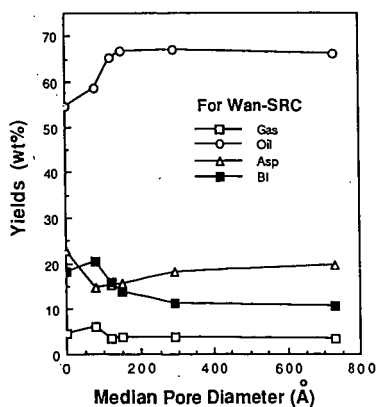


Figure 7. Effect of catalyst pore size on hydroprocessing of unfractionated SRC (Wan-SRC)

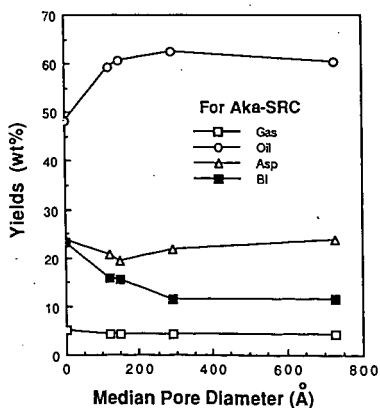


Figure 8. Effect of catalyst pore size on hydroprocessing of unfractionated SRC (Aka-SRC)

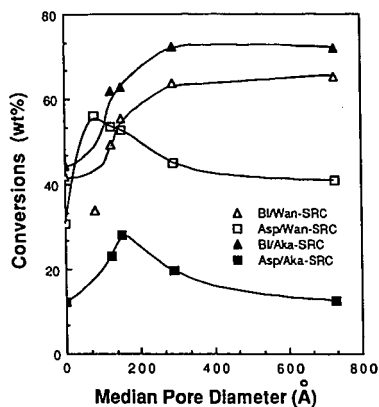


Figure 9. Effect of catalyst pore size on net conversion of asphaltene and preasphaltene in SRC hydroprocessing

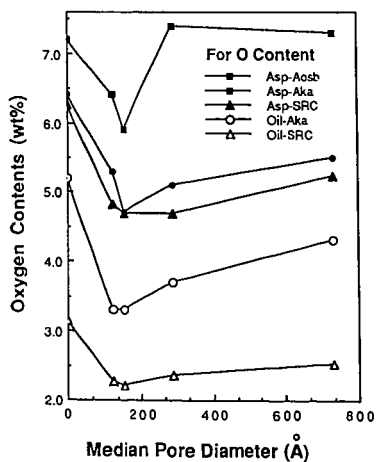


Figure 10. Effect of catalyst pore size on oxygen removal

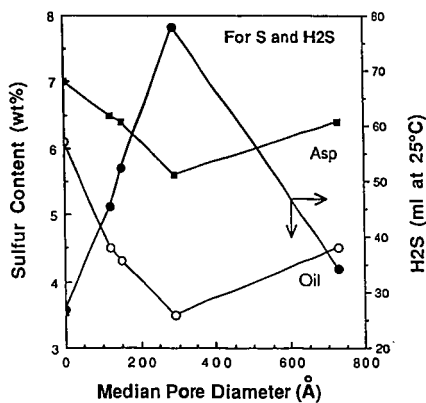


Figure 11. Effect of catalyst pore size on the removal of sulfur from the bitumen asphaltene